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(21) International Application Number: PCT/US98/12047 (22) International Filing Date: 9 June 1998 (09.06.98) (30) Priority Data: 08/872,616 10 June 1997 (10.06.97) US (63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application US 08/872,616 (CIP) Filed on 10 June 1997 (10.06.97) (71) Applicant (for all designated States except US): MONSANTO COMPANY [US/US]; 800 N. Lindbergh Boulevard, St. Louis, MO 63167 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): COLEMAN, James, P. [GB/US]; 2374 Wesecreek Drive, St. Louis, MO 63043 (US). (74) Agents: CASSEL, Alan, L. et al.; Howell & Haferkamp, L.C., Suite 1400, 7733 Forsyth Boulevard, St. Louis, MO 63105 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	

A cross-sectional view of a multi-layered device 10. The device consists of a top layer 12, a middle layer 14, and a bottom layer 14'. The middle layer 14 contains a series of rectangular blocks 16. The top layer 12 has a central opening 18. The bottom layer 14' has a central opening 20. The middle layer 14 has a central opening 22. The top layer 12 is labeled 10. The middle layer 14 is labeled 14. The bottom layer 14' is labeled 14'. The central opening 18 is labeled 18. The central opening 20 is labeled 20. The central opening 22 is labeled 22. The rectangular blocks 16 are labeled 16. The top layer 12 is labeled 12. The middle layer 14 is labeled 14. The bottom layer 14' is labeled 14'.

An electrochromic display having an image including fine detail may be produced by applying working (14) and counter (14') electrodes on one side of a nonconductive substrate (12), applying conductive coatings (16) on the electrodes, and printing an image (20) over one or both of the conductive coatings covering the electrodes using an ink containing an electrochromic substance. The electrodes (including the area covered by the electrochromic substance) are then bridged with an ionically conductive coating (28). In a preferred arrangement, the two conductive coatings (16) may merge into a single coating bridging a gap (22) between the electrodes. Prussian blue can be used as a pigment in the electrochromic ink. Complementary electrochromic materials may be printed over both electrodes, more than one electrochromic material may be printed on a single electrode, and various pigments (including fluorescent pigments) may be mixed with the electrochromic materials to obtain various special effects.

SWITCHABLE IMAGES WITH FINE DETAIL

## BACKGROUND OF THE INVENTION

## 1. Field of the invention

Disclosed herein are novel electrochromic devices having finely detailed switchable images, characterized in part in having a working electrode having a surface with portions having different electrochromic properties, wherein the surface portions and electrochromic properties may be selected to present an electrochromically switchable, finely detailed image over the surface of the working electrode.

## 2. Description of the prior art

Inaba et al. (U.S. Patent No. 4,850,684) is directed to an electrochromic display comprising a display electrode made up of a transparent conductive layer and a patterned EC layer, a counter electrode having an EC layer laid on a conductive layer and an electrolyte which occupies the space between the two electrodes, and in which the display electrode employs a first type EC material that takes on color in its electrochemically oxidized state, such as Prussian blue, and the counter electrode a second type EC material that

takes on color in its reduced state, such as WO<sub>3</sub>, or vice versa. The reference is primarily directed to transmissive-type EC display devices requiring transparent electrodes, although a reflection board may be placed outside the display device cell or in the electrolyte liquid in a reflective type EC display.

Devices made in accordance with Inaba et al., however, require a counterelectrode which is arranged opposite to and spaced from the display electrode, with an electrolyte liquid occupying the space between the counter electrode and the display electrode. Moreover, the counterelectrode must be coated with a substantially larger amount of EC material than the display electrode. Thus, devices made in accordance with the teachings of Inaba et al. require two coated surfaces, and electrical contacts on two surfaces. Because electrical contacts are made to two opposing surfaces, the surfaces must be sufficiently rigid to prevent their contacting one another, unless insulating spacers, e.g., glass balls, are used. Furthermore, because two different types of EC materials must be used on the electrodes, an initial reduction treatment of both materials is necessary, and to accomplish this treatment, an additional electrode is required.

Wada et al. (U.S. Patent No. 4,375,319) discloses an electrochromic display in which an electrode is formed by depositing electrochromic material into a required configuration on a transparent conductive film in which a portion of the film is contacted by the electrochromic material and another portion constitutes a lead extension for connection to an electrical circuit. Because an exposed portion of the conductive film can be chemically attacked during actuation of the display device, a film must be provided over a portion of the conductive material not covered by the EC material, and the display

is viewed through the transparent conductive film upon which the EC material is placed. A separate, opposing counterelectrode coated with a protective layer (usually of EC material) is required on a separate substrate, as is a separate reference electrode. It is not suggested that EC material be printed on an opaque electrode, and that both the printed EC material and a counterelectrode be applied to the same substrate layer.

It would therefore be advantageous if a method were available for producing detailed images in an electrochromic display that required electrodes and EC material on only one side of a single substrate. It would also be advantageous if such a method of producing such a display did not require a rigid substrate, so that the display could be produced more conveniently.

It would also be advantageous if an electrochromic display could be provided that required neither pre-bleaching nor the additional electrode required to accomplish such pre-bleaching. It would further be advantageous to have available electrochromic displays that are capable of displaying fine details of line drawings, printed words, and half-tone pictures and that are easily manufacturable.

It would also be advantageous if a display were available in which the EC material was printed on an electrode that matched the color of the EC material when the EC material is in a first oxidation state, and that contrasted with the color of the EC material when the EC material is in a second oxidation state, so that the image could appear to be switched on and off relative to a background.

#### BRIEF DESCRIPTION OF THE INVENTION

According to one aspect of the invention, a method for printing detailed electrochromic image is provided in

which first, a working electrode is printed on one side of a film, such as a mylar film. A counterelectrode is also printed on the same side of the film surrounding the working electrode, the counterelectrode preferably being approximately equal in total area to the working electrode. Both electrodes are then coated with electrically conductive, stable material having little or no electrochromic properties. The resulting surface should be light-colored, although other colors are possible, depending upon the electrochromic pigment applied in a later step. The desired image is then printed onto the surface of the working electrode, preferably using a dispersion of a good electrochromic material in a polymer binder, although other methods of applying the electrochromic material are possible.

The counterelectrode may be optionally printed with the same or some other material to act as an additional sink and/or source for electrons. A layer of electrolyte is then applied over both electrodes and optionally sealed with a clear film.

Providing that the background color of the working electrode coating is closely color-matched to one state of the electrochromic material from which the image is printed, the image may be displayed or erased by applying a suitable positive or negative DC voltage. It may be desirable in other applications to provide a detailed image that switches from one color to a second, where both colors contrast to a greater or lesser degree with the background color. It is possible to provide an attractive, detailed, attention-getting display, for example, by printing, on an electrode, a mixture of an electrochromic chemical and a fluorescent pigment in a desired pattern.

It is thus an object of the invention to provide an electrochromic display that is capable of switching

display elements having fine detail and that allows all of the necessary electrodes to be printed on a single side of one surface.

5 It is a further object of the invention to provide an electrochromic display that is capable of switching display elements having fine detail and that requires only two electrodes.

10 It is an additional object of the invention to provide an electrochromic display that is capable of switching display elements having fine detail and that can be produced conveniently without requiring a rigid substrate.

15 It is yet another object of the invention to provide an electrochromic display that is capable of switching display elements having fine detail and that does not require either pre-bleaching or the additional electrode required to accomplish such pre-bleaching.

20 It is still another object of the invention to provide an electrochromic display that is capable of switching display elements having fine detail and that provides a background for the display elements that can closely match the color of the electrochromic display elements when the electrochromic material in the display elements is in a first oxidation state, and that  
25 contrasts with the color of the electrochromic material in the display elements when it is in a second oxidation state, so that the image appears to be switched on and off relative to the image's background when an appropriate electric charge is injected into the display  
30 through the display's electrodes.

It is a still further object of the invention to provide methods for producing displays having the above-described advantages.

35 These and other objects of the invention will be recognized, understood, and appreciated by one skilled in

the art upon reading the accompanying description of this invention.

#### BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a drawing of a cross-section of an electrochromic display in accordance with this invention;

Figure 2 is a drawing of a working electrode and counterelectrode in proximity to one another in accordance with the invention;

Figure 3 is a drawing of a first test image used for printing electrochromic material on a working electrode in accordance with the invention;

Figure 4 is a drawing of a second test image used for printing electrochromic material on a working electrode in accordance with the invention;

Figure 5 is a drawing of a third test image used for printing electrochromic material on a working electrode in accordance with the invention;

Figure 6 is a drawing of a fourth test image used for printing electrochromic material on a working electrode in accordance with the invention; and

Figure 7 is a drawing of a fifth test image used for printing electrochromic material on a working electrode in accordance with the invention.

It should not be assumed that the figures are necessarily drawn to scale.

#### DETAILED DESCRIPTION OF THE INVENTION

Percentages expressed herein as "%" are mole percent unless indicated otherwise, e.g. weight percent is expressed as "wt%".

As used herein the terms "oxidized" and "reduced" mean changing the number of electrons associated with a valence state of a material by chemical or electrochemical means. An oxidized metal oxide is a material that has fewer electrons than the same metal oxide material in its natural state. Conversely, a

reduced metal oxide is a material that has more electrons than the same metal oxide material in its natural state. A common chemical reducing agent is sodium borohydride which is capable of putting electrons accompanied by  
5 ions, e.g. protons or other cations such as sodium, lithium, etc., into a tin oxide lattice. In a reduced state, e.g. when saturated with electrons, doped tin oxide has a darker color and lower conductivity. Interestingly, the conductivity of both reduced and  
10 oxidized doped tin oxide is significantly lower than the conductivity of doped tin oxide in the natural state. The conductivity of oxidized doped tin oxide is lower because the number of electron carriers is substantially lower. The conductivity of reduced doped tin oxide is  
15 lower because the material is so saturated with electrons that electron mobility is impaired. To achieve an electrochromic effect it is believed that it is necessary to cause an electrochromic-generating oxidation or reduction at the surface of the electrochromic material,  
20 e.g. typically by applying an electrical potential of 1 volt or less to cause cations and electrons to migrate into or out of the surface layer of the electrochromic material.

As used herein the term "contrast ratio" (CR)  
25 describes the difference in color of a material in oxidized and reduced states. More particularly, contrast ratio means the ratio of reflectance of a material in an electrochemically oxidized state to the reflectance of the material in an electrochemically reduced state, where  
30 reflectance is a photo diode measurement of the value of light reflected off the oxidized or reduced material from a constant source of light shining on the material. A material having a  $CR = 1$  would have no electrochromic effect, that is the light reflected from the material in  
35 a reduced state would be immeasurably different from the



light reflected from the material in an oxidized state. The magnitude of the contrast ratios of the color changes in the examples in this description were determined by fitting an electrochromic display device having the specified pigments under a microscope fitted with a  
5 Melles-Griot photodiode wide band width amplifier. The output voltages measured from the amplifier are proportional to the reflectance of the pigment. The contrast ratio is thus determined by the ratio of the  
10 output voltages measured in the pigment's distinct electrochromic oxidation states.

A material is said to be in an oxidized state when it has fewer electrons than in the reduced state. For instance, in oxides, antimony has two stable oxidation  
15 states with two or zero electrons in the outer shell. These are denoted as Sb(III) and Sb(V). In the mixed oxide compound antimony tin oxide (ATO), as naturally formed, the antimony atoms in the metal oxide lattice are at an oxidation state intermediate between III and V with  
20 electrons from the antimony in a tin 5s electron orbital based conduction band. In ATO the natural blue grey color is believed to be due to a charge transfer absorption band.

As used herein, a non-reactive, electrochemically  
25 inactive (which, for purposes of this specification, may therefore be called "inert") pigment is a pigment that does not react with the chemicals of the electrochromic display of which it is a part, and does not participate in any redox reaction caused by the application of a  
30 normal electrochromic switching voltage to the display.

Referring now to Figure 1, an electrochromic display 10 in accordance with the invention comprises working electrode 14 sufficient to encompass the overall size and shape of the desired image outline is printed  
35 with silver ink or another suitable substance on a

nonconducting film 12, such as mylar film. Although the film 12 is preferably a flexible material, a rigid, nonconducting, printable material such as glass may be used to achieve at least some of the objects of the invention. The working electrode 14 is surrounded by a counterelectrode 14' of approximately equal area. Because the electrochromic effect of devices in accordance with the invention may be observed without looking through the printed film, neither the film 12 nor the conductive electrodes 14, 14' need be transparent or translucent, and highly conductive, but nontransparent, electrodes, such as silver, may advantageously be used. Figure 2 is a drawing showing the approximate relationship of the working electrode 14 and counterelectrode 14' in one of many possible configurations, with Figure 1 being a profile view and Figure 2 being a view of the electrodes through film 12. A portion of the working electrode 14 and counterelectrode 14' may be run off as leads 24 and 24', respectively, each connected to a conveniently located contact pad, 26 and 26', respectively, for connection to a power source.

Returning now to Figure 1, a carbon coating 16, 16' may optionally be applied to all or any portion of electrodes 14, 14' (respectively) to provide corrosion protection. The carbon coating 16, 16' preferably covers all of the corresponding electrode 14 or 14', and, although not shown in Figure 1, may "spill over" into gap areas 22 to provide edge protection of the corresponding electrodes, but the carbon coatings 16 and 16' must not be electrically short circuited to one another. (Leads 24 and 24', not shown in Figure 1, may instead be covered with an insulating and/or protective film, if desired, while contact pads 26 and 26', also not shown in Figure 1, may be bare or otherwise treated for the best external

electrical connection.) Both electrodes 14 and 14' (or the optional carbon coating 16 and 16' on top of them) are then coated with a dispersion 18 of a light-colored, conductive pigment such as ATO-TiO<sub>2</sub> (e.g., Mitsubishi W-1, which is a light grey conductive powder comprising 12.25% ATO on 0.2 micron TiO<sub>2</sub> particles in the weight ratio of 23:77) in an elastomer such as VITON fluoro-elastomer to give a light-colored electrode surface with little or no electrochromic properties. Other materials giving a stable electrode surface with no electrochromic properties may also be used as a coating material, such as indium-tin oxide dispersions. The surface coating 18 may optionally bridge the gap 22 between the working electrode 14 and the counterelectrode 14', although, as explained below, such bridging tends to slightly degrade the performance of the display 10. However, it has been found by experiment that the degradation is significant only when the color produced in the display is required to be stable for periods of about 12 hours or more without an external power source being connected to the electrodes 14 and 14'. On the other hand, displays with a bridged surface coating 18 do not require alignment of the surface coating pattern with the electrodes 14 and 14', and a coating 18 that is visually continuous can result in a more aesthetically pleasing display.

The desired image 20 is then printed onto the surface of the coating 18 over the working electrode 14. The printed image 20 comprises a dispersion of a good electrochromic material in a polymer binder, e.g., Prussian blue coated onto DuPont "ZELEC" 1703-S ATO-silica particles, dispersed in a fluoroelastomer binder. For example, a pigment made from Prussian blue coated onto DuPont ECP1703S (ATO on hollow silica shells of 9 micron average particle size, containing 65 wt. % ATO [which itself is 3.8 mole % Sb and 96.2 mole % Sn] and

wt. % silica) may be made into a suitable ink using Acheson Colloids SS24932 fluoroelastomer binder. Optionally, the counterelectrode 16' may be printed with the same or some other material to act as an additional sink and/or source for electrons. A layer of an electrolyte 28 is then applied over both electrodes 14 and 14' and the display 10 is optionally sealed with a clear protective cover 30, such as a clear film.

Providing that the background color of the working electrode coating 18 is closely color-matched to one state of the electrochromic material from which the image 20 is printed, the image on the working electrode may be displayed or erased by applying a suitable positive or negative DC voltage to the working electrode 14 relative to the counterelectrode 14'. Thus, images in the form of words, line drawings, or "halftone" pictures printed with dots may be printed in switchable form with this invention. Because electrochromic material may be printed on the counterelectrode as well, a second image may be printed in switchable form that is displayed only when the first image is switched off. Although desirable for many applications, it is also not necessary that the printed electrochromic image match the background so closely as to appear to be switched on and off. Other effects are possible, such as having the electrochromic image change from a first color to a different, contrasting color.

Various printing methods may be used to apply the printed electrochromic image, such as lithography, silkscreening, rotogravure, photogravure, and flexographic printing. It is also possible to apply the electrochromic image with numerous other methods besides printing, such as sputtering or evaporation through a mask.

Without wishing to be bound by any particular

theory of operation, the surprising uniformity of electrochromic switching across the printed portion of the coated electrode surface is believed to be enhanced by both the relatively high conductance of the electrode itself as well as the relatively low conductance of the non-electrochromic coating over the electrode. It is believed that the resistance of the coating tends to enhance the electric field near the center of the electrode when a voltage is initially applied to it, thereby enhancing the color change of electrochromic material that is printed near the center of the electrode. Without a relatively low conductance coating over the electrode, it is believed that most of the electric field would be concentrated in and near the gap between the working electrode and counterelectrode, and that the electrochromic effect would tend to be concentrated in electrochromic material printed near the edges of the working electrode.

It is further believed that the high lateral conductivity of the electrode under the relatively low conductance coating serves to equalize charge over the surface of the coating when the external power supply is removed, thereby enhancing the spreading of the electrochromic effect over the entire printed region of the electrode. For example, the lateral conductivity of a typical silver film such as those used in the examples is about 30-50 milliohms per square, whereas that of an ATO film would be about 10-50 Kiloohms per square. This higher conductivity of the silver electrode tends to rapidly equalize electrical charge over the printed surface of the coating when the external power supply is removed, even though there may be a higher resistance carbon layer between the silver electrode and the coating, because the carbon layer is thin and thus has a very low vertical resistance.

As mentioned above, it has been found desirable, from an electrical if not an aesthetic standpoint, not to bridge the gap 22 between the working electrode 14 and the counterelectrode 14' with the relatively high resistance coating 18 (e.g., the ATO coating). Doing so creates a relatively low resistance short-circuit (about 600 to 4000 ohms, as measured in some of the displays described in the examples below) between the electrodes. The resistance depends upon the width of the gap, the total length of the gap, and the thickness and inherent resistance of the coating, but was measured at between about 600 and 4000 ohms for the specific displays described in the examples below. The charge leakage between the electrodes 14 and 14' due to this resistance will reduce the persistence of any electrochromic image that is formed on the printed electrode 14 after power is removed from the display. However, even with this charge leakage, it is believed that the electrochromic effect may persist for a few hours or more. Therefore, for most applications, it is anticipated that the additional alignment step that would be required to avoid placing the coating over the interelectrode gap combined with what may be considered to be a more aesthetically pleasing appearance of a continuous, gap-free background, would outweigh the advantages of increasing the persistence of the display beyond 12 hours.

Preferably, the electrochromic material should be a material that switches at a relatively low voltage, such as Prussian blue, particularly if large printed picture elements 20 are to be switched. It has been observed that the uniformity enhancement of the electrochromic effect in displays according to the invention is reduced when higher-voltage electrochromic materials are used.

## EXAMPLE I

To test the inventive concepts, screens were produced for printing images onto standard one-inch test squares, printed over carbon-coated silver electrodes. These images included a word display (illustrated in Figure 3), cartoon line drawings (illustrated in Figures 4 and 5), and a halftone dot pattern (illustrated in Figure 6). The screens for these images were used to test the printing of images with an ink made from Mitsui Passtran 5210. Passtran 5210 is a grey conductive powder of 11.5% ATO on 4 micron aluminum borate particles in the weight ratio of 54:46 with a contrast ratio greater than 4. The powder is dispersed in a fluorinated elastomer dissolved at 22 weight percent (wt%) in butoxyethyl acetate. Sufficient Passtran 5210 dispersed in the elastomer solution so that the weight ratio of ATO-coated powder to elastomer was 2.5:1. The images were reproduced very accurately.

## EXAMPLE II

Prussian blue ink was prepared by dissolving 6 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in 1.5 liters of deionized water and slurrying into the resulting solution 151 g of duPont Zelec ECP 1703-S (lot 47630). A solution of 4.5 g  $\text{K}_3\text{Fe}(\text{CN})_6$  in 225 ml of deionized water was added dropwise to the well-stirred slurry. The resulting blue slurry was stirred a few minutes and then vacuum filtered. The filtrate is nearly colorless. The filter cake was pressed repeatedly with a spatula to remove as much water as possible. The combined filter cakes from three identical batches were dried in a vacuum oven at 60°C. After drying for several days, the resulting lumpy powder was gently ground with a large mortar and pestle and made into an ink by dispersing it in 22% fluoroelastomer in a manner similar to that described in Example I.

A screen similar to that which was used in Example I was used to print the Prussian blue ink onto W-1 squares. When covered with an electrolyte and  $\pm 1.5$  volts applied, the images turned from dark blue to light gray. When potassium formate electrolyte was used, the gray state of the screened image nearly matched the gray of the W-1 background so that the image appeared to switch from blue to nothing. When a KCl electrolyte was used, the gray state of the printed image was darker than that of W-1, so the image switched from blue to gray. Other similar images were screen printed using mixtures of Prussian blue and fluorescent pigment inks, as indicated in Table 1. These resulted in completed displays which had images switching from one color to another, e.g., chocolate to orange, green to yellow, and violet to rose.



TABLE 1

	Pigment Composition	Electrolyte Composition	Color Change
5	Prussian Blue + "HIVIZ®" TS14 fluorescent orange pigment	KCl solution	chocolate → orange (slow)
10	Same as preceding example, but thinner ink (less pigment)	KCl solution	slate → orange/tan (faster)
15	Prussian Blue layer printed over "HIVIZ®" TS13/DuPont 1703S layer	KCl Solution	patchy blue → gray or orange
	HM-13/Prussian Blue	KCl Solution	dark lavender → rose
20	Prussian Blue train over Mitsui W-1 electrode	Potassium formate solution	blue → gray (invisible, train blends into background)
	Prussian Blue: "HIVIZ®" TS13 2:1	KCl solution	deep violet → light rose
25	Prussian Blue: HM13 <sup>1</sup>	KCl solution	blue switches but red color eventually fades

<sup>1</sup> HM13 is a "rocket red" pigment from Day-Glo Color Corp., Cleveland, Ohio.

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## EXAMPLE III

For a print run, a picture of a shark was translated into halftone form, as shown in Figure 7. A working electrode and counterelectrode were designed to fit the shark image. The device was printed with Prussian blue ink on top of a Mitsui W-1 electrode. Applying electrolyte (e.g., KCl solution, thickened with agar) and  $\pm 1.5$  volts, the shark image changed from dark blue to almost invisible light gray.

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## EXAMPLE IV

A halftone Prussian blue shark was coated with KCl/hydroxyethylcellulose (HEC) electrolyte, sealed and switched overnight with a 50 milliHertz,  $\pm 1.2$  volt square wave. The blue dots of the shark turned gray but did not disappear into the W-1 background. Thus, the shark appeared to change from deep blue to light gray. Other examples are given in Table 2.

15

TABLE 2

Pigment	Electrolyte	Colors
Prussian Blue (shark)	KCl/HEC	blue → gray (shark always visible)
Prussian Blue (shark)	LiCl/HEC	blue → gray yellow (shark always visible)
Prussian Blue (shark)	Potassium Formate /POLYAMPS <sup>2</sup>	blue → gray (shark always visible)
4:1 Prussian Blue: "HIVIZ®" TS14 (train)	KCl	dark brown → dirty orange
Prussian Blue (halftone)	potassium formate	blue → dark gray
4:1 PB: "HIVIZ®" TS14 (train)	potassium formate	brown → bright orange

The specific examples recited above are intended only to illustrate the invention and its practical application, and are not intended to be limiting. Many modifications, still in keeping within the scope and spirit of the invention, will be apparent to one skilled in the art upon reading this description. Therefore, the scope of the invention should be interpreted by reference to the claims below, including their full range of equivalents under applicable law.

<sup>2</sup>Polyacrylamidomethyl-propanesulfonate polymeric gel.

## WHAT IS CLAIMED IS:

1. A method of producing an electrochromic display having an image including fine detail, the method comprising the steps of:

5       applying a working electrode on a first side of a nonconductive substrate;

      applying a counter electrode on the first side of the nonconductive substrate;

      applying a first conductive coating on the working electrode;

10       applying a second conductive coating on the counter electrode;

      applying a pattern of a first electrochromic material over at least a portion of said first conductive coating; and

15       bridging the first electrochromic material and at least a portion of the second conductive coating with an ionically conductive electrolyte;

      wherein the second conductive coating comprises a material electrically complementary to the first  
20       electrochromic material.

2. The method of claim 1, wherein the second conductive coating is applied to an area of the substrate not more than 2.0 nor less than 0.5 times the area of the substrate to which the working electrode is applied.

3. The method of claim 1, wherein at least one of the steps of applying the working electrode and applying the counter electrode comprises the steps of:

5       applying a metal film on one side of the nonconductive substrate; and

      applying a carbon coating over the metal film.

4. The method of claim 3, wherein the metal film is

applied in a thickness such that it has a resistance of between about 30 and about 50 milliohms per square.

5        5.        The method of claim 4, wherein at least one of the first and the second conductive coatings comprises a material having a lower conductivity than the metal film, and is applied over the carbon coating in a thickness having a resistance of between about 10 and about 50 kilohms per square.

6.        The method of claim 1 wherein at least one of the applying steps is performed by a printing process.

7.        The method of claim 6, wherein the printing process is silkscreening.

8.        The method of claim 6, wherein the printing process is rotogravure.

9.        The method of claim 6, wherein the printing process is lithography.

10.       The method of claim 6, wherein the printing process is photogravure.

11.       The method of claim 6, wherein the printing process is flexography.

5        12.       The method of claim 1, wherein the first electrically conductive coating and the second electrically conductive coating comprise the same materials and are applied as a single continuous coating bridging a gap between the working electrode and the counter electrode.

13. The method of claim 12, wherein the single continuous coating is applied to produce a resistance of between about 600 and about 4000 ohms between the working electrode and the counter electrode.

14. The method of claim 1, wherein the first electrochromic material comprises Prussian blue.

5 15. The method of claim 1, wherein the first electrochromic material and the first conductive coating are selected to have essentially identical colors in at least one oxidation state of the first electrochromic material.

16. The method of claim 1 and further comprising the steps of:

5 applying a second pattern of a second electrochromic material over the second conductive material; and

bridging the second pattern of electrochromic material and at least a portion of the first conductive coating with the ionically conductive electrolyte.

17. The method of claim 16 wherein the second pattern of electrochromic material and the first pattern of electrochromic material comprise the same electrochromic material.

18. The method of claim 1 and further comprising the steps of:

5 applying a second pattern of electrochromic material over the first conductive material; and  
bridging the second pattern of electrochromic material and at least a portion of the second conductive coating with the ionically conductive electrolyte;

wherein the second pattern of electrochromic material and the first pattern of electrochromic material comprise different electrochromic materials.

19. An electrochromic device comprising:
- a nonconductive substrate;
  - a conductive working electrode on a face of the nonconductive substrate;
  - a conductive counter electrode also on the face of the nonconductive substrate;
  - a first conductive coating on the working electrode;
  - a second conductive coating on the counter electrode;
  - a pattern of a first electrochromic material over at least a portion of the first conductive coating, the electrochromic material being electrically complementary to the second conductive coating; and
  - a layer of ionically conductive electrolyte overlaying at least a portion of each of the pattern of the first electrochromic material and the second conductive coating and providing ionic conduction therebetween.

20. The device of claim 19 wherein the second conductive coating has an area not more than 2.0 nor less than 0.5 times the area of the working electrode.

21. The device of claim 19 wherein at least one of the working electrode and the counter electrode comprises a metal film on one side of the nonconductive substrate which is overlaid by a carbon coating.

22. The device of claim 21 wherein the metal film has a resistance of between about 30 and about 50 milliohms

per square.

23. The device of claim 22 wherein one of the first and the second conductive coatings overlays the metal film and has a resistance of between 10 and about 50 kilohms per square.

24. The device of claim 19, wherein the first electrically conductive coating and the second electrically conductive coating comprise the same materials and bridge a gap between the working electrode and the counter electrode.

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25. The device of claim 24, wherein a resistance between the working electrode and the counter electrode is between about 600 and about 4000 ohms.

26. The device of claim 19, wherein the first electrochromic material comprises Prussian blue.

27. The device of claim 19, wherein the first electrochromic material and the first conductive coating have essentially identical colors in at least one oxidation state of the first electrochromic material.

28. The device of claim 19 and further comprising a second pattern of electrochromic material over the second conductive material, and wherein the layer of electrolyte also covers at least a portion of the second pattern of electrochromic material.

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29. The device of claim 28 in which the electrochromic materials in the first pattern of electrochromic material and in the second pattern of electrochromic material is the same.



5        30.        The device of claim 19 and further comprising a second pattern of electrochromic material over the first conductive material, wherein the layer of electrolyte also covers at least a portion of the second pattern of electrochromic material and wherein the first pattern of electrochromic material and second pattern of electrochromic material comprise different electrochromic materials.

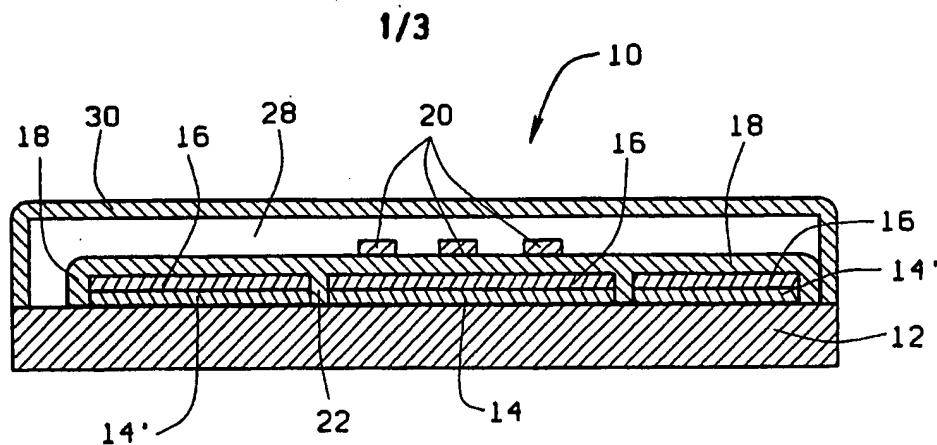


FIG. 1

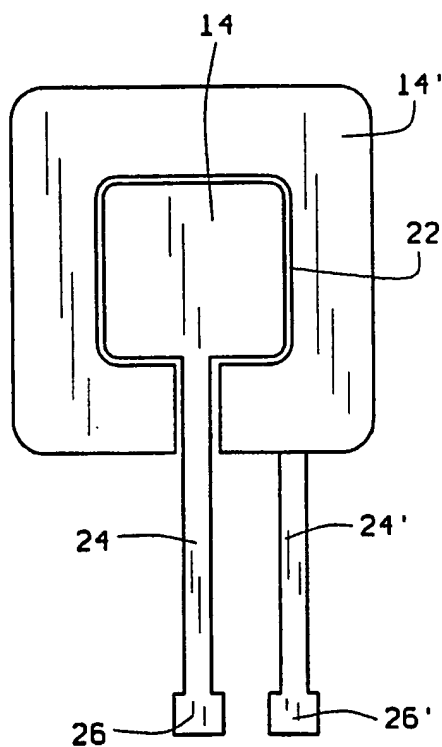


FIG. 2

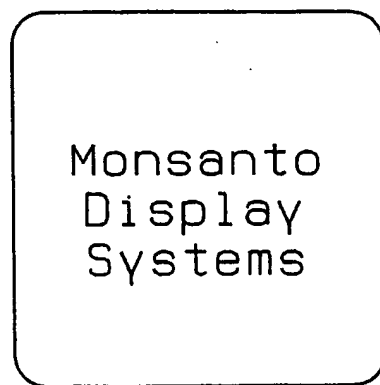


FIG. 3

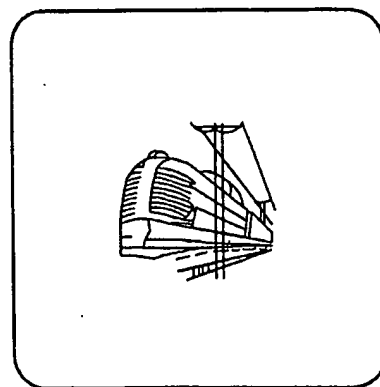


FIG. 4

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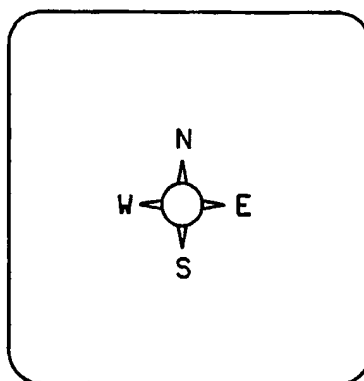


FIG. 5

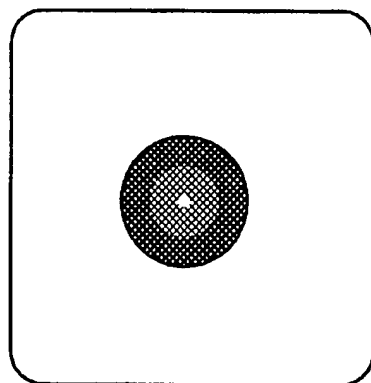


FIG. 6

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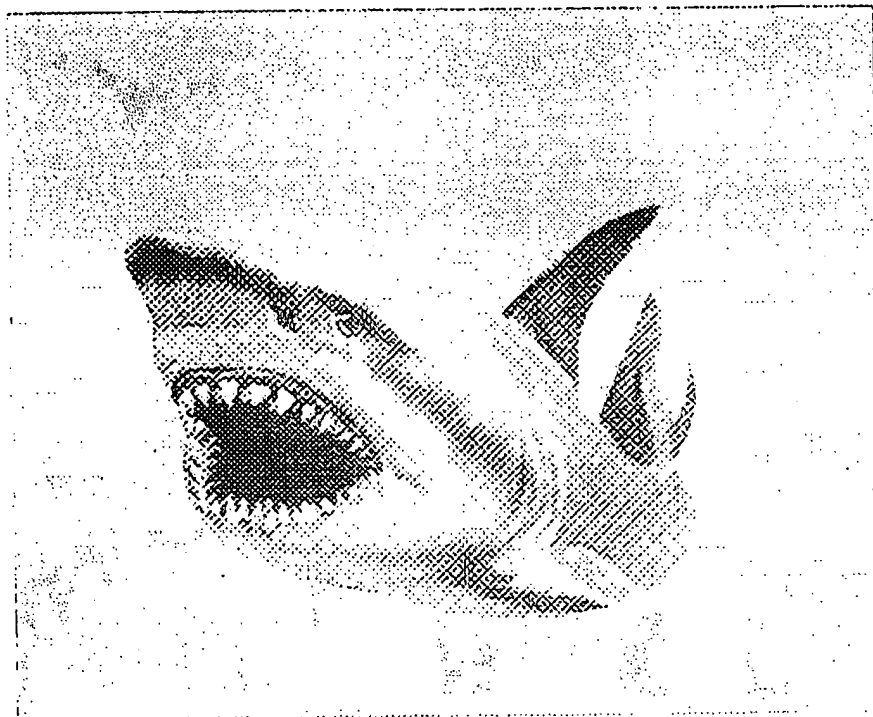


FIG. 7

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/12047

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 G02F1/155 G02F1/153

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 91 13381 A (MOLECULAR DISPLAYS INC) 5 September 1991 see page 6, line 8 - line 19 see page 17, line 12 - page 18, line 29 see page 22, line 4 - line 24; figure 6 ---	1, 19, 30
A	WO 94 15246 A (MONSANTO CO ; COLEMAN JAMES PATRICK (US)) 7 July 1994 see page 3, line 6 - page 7, line 21 see page 9, line 22 - line 30 see page 10, line 23 - page 11, line 8 see page 13, line 22 - page 14, line 7 see page 16, line 32 - page 18, line 25; figures 1-6; examples 6,7 --- -/--	1-6, 12-29

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

30 September 1998

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07/10/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

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## INTERNATIONAL SEARCH REPORT

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PCT/US 98/12047

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	OREL B ET AL: "Electrochemical and structural properties of SnO <sub>2</sub> and Sb:SnO <sub>2</sub> transparent electrodes with mixed electronically conductive and ion-storage characteristics" JOURNAL OF THE ELECTROCHEMICAL SOCIETY, vol. 141, no. 9, 1 September 1994, pages L127-130, XP000469412 see page L129, right-hand column, line 12 - line 25  -----	1,19

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